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An Approximate Analysis of Simultaneous
Gas-Phase and Surface Atom Recombination
for Stagnation Boundary Layer

26 NOVEMBER 1962

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Aerodynamics and Propulsion Research Laboratory

Prepared for COMMANDER SPACE SYSTEMS DIVISION
UNITED STATES AIR FORCE
Inglewood, California



LABORATORIES DIVISION • AEROSPACE CORPORATION
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ABSTRACT

The concept of equivalent surface reaction is developed for gas-phase recombination at the stagnation region of blunt bodies. This concept is based on the fact that the chemical state of a nonequilibrium highly cooled boundary layer is largely determined by the recombination that occurs near the wall. An equation based on this concept is shown to predict the heat transfer to a noncatalytic surface to within a few percent of the more accurate existing results. The equation is generalized to apply to the case in which surface catalytic recombination occurs simultaneously with gas-phase reaction.

INTRODUCTION

The chemical state of nonequilibrium boundary layers about hypersonic vehicles is of considerable interest. The interest stems mainly from the fact that the heat transfer to the body, and the observables in the wake and the trails, are greatly affected by the chemical state of the boundary layers.

The problem of nonequilibrium chemically recombining boundary layers is a formidable one and exact solutions are available only for a few special cases. The solutions that exist have been obtained by assuming that either the gas phase or the surface recombination occurs alone.^{1-6*} At this stage of development, an approximate solution will be useful if it takes reasonable account of the simultaneous effects of gas phase and surface recombination.

It has been shown⁷ that the chemical state of the boundary layer is controlled mainly by the recombination which takes place near the wall when the wall is highly cooled. This observation suggests representing the gas phase reaction by an equivalent surface reaction with all state variables specified by surface conditions. The order of reaction and the corresponding rate constant of this equivalent surface reaction will be determined for a noncatalytic wall. The equivalent surface reaction concept will then be extended to the case in which the surface has an arbitrary catalycity.

The basic concept of emphasizing the region of maximum chemical activity in determining the chemical state of the boundary layer was first used by Rae⁸ for the boundary layer in which dissociative reactions predominate.

ANALYSIS

Fay and Riddell¹ have obtained an exact solution of the nonequilibrium stagnation point boundary layer with the chemical state of the gas in the boundary layer ranging from frozen to equilibrium. The computations were for a noncatalytic wall at a temperature of 300°K and for a selected flight condition. Chung and Anderson² have calculated by an integral method the

*Numbers indicate References at the end of paper.

nonequilibrium effect on heat transfer to blunt cones with noncatalytic walls at temperatures of 1000 and 1500°K for two flight conditions. Goodwin and Chung⁹ have successfully obtained additional solutions and have correlated the results for various flight conditions and a wall temperature of 1500°K by a single recombination rate parameter.

Subsequently, Inger⁷ has shown that the difference in wall temperature between the two theoretical solutions^{1, 2, 9} may be included in the correlation by noting the controlling influence of the wall temperature upon the chemical state of the boundary layer. It appears that, with the resulting comprehensive correlation, the essential effects of nonequilibrium reaction on chemical state and heat transfer have been taken into account, at least to the correct order of magnitude.

The order and rate constant for the proposed equivalent surface reaction will be determined first for noncatalytic walls. Since the gas phase reaction near the surface of a highly cooled hypersonic vehicle is predominantly that of recombination requiring three body collisions, a modified second order reaction appears to be a reasonable choice for the equivalent surface reaction. We let

$$\rho_w D_w \left(\frac{\partial m}{\partial y} \right)_w = K_g \frac{m_w^2}{1 + m_w} \quad (1)$$

where K_g is the equivalent surface reaction constant for the gas phase reaction. The constant K_g is to be determined subsequently. In effect, we are assuming that the nonequilibrium gas phase reaction over a noncatalytic wall is equivalent to a frozen boundary layer with the surface reaction specified by Eq. (1).

An exact solution of the diffusion equation at the stagnation point³ gives the following equation for a frozen boundary layer

$$\left(\frac{\partial m}{\partial \eta} \right)_w = 0.47(1 - m_w) Sc^{1/3} \quad (2)$$

where

$$\begin{aligned}\eta &= \frac{u_e r^\epsilon}{(2Cs)^{1/2}} \int_0^y \rho dy \\ s &= \int_0^x \rho_e \mu_e u_e r^{2\epsilon} dx \\ C &= \left(\frac{\rho \mu}{\rho_e \mu_e} \right)_0 = \text{constant}\end{aligned}\quad (3)$$

Solution of Eqs. (1) and (2) for m_w gives*

$$m_w = \sqrt{\frac{1}{1 + \hat{K}_g}} \quad (4)$$

where

$$\hat{K}_g = \frac{Sc^{2/3}}{(0.47)\sqrt{(1+\epsilon)(\rho_e \mu_e)_0} \beta C} K_g \quad (5)$$

For the Lewis number not much different from one, it can be readily shown that

$$\frac{q - q_f}{q_E - q_f} = 1 - m_w \quad (6)$$

Equations (4) and (6) give at the stagnation point

$$\frac{q - q_f}{q_E - q_f} = 1 - \sqrt{\frac{1}{1 + \hat{K}_g}} \quad (7)$$

* For the stagnation region:

$$\begin{aligned}u_e &= \beta x \\ r &= x\end{aligned}$$

Solutions of nonequilibrium boundary layers exist for axisymmetric bodies only. The following correlations, therefore, will be limited to the stagnation regions of axisymmetric bodies. The correlation of Goodwin and Chung⁹ including the surface temperature correlation of Inger⁷ gives $(q - q_f)/(q_E - q_f)$ in terms of a single parameter:

$$\Gamma_g = \frac{1}{\beta} (2k_o) \frac{1}{(T_{eo})^{3.5}} \left(\frac{p}{R}\right)^2 \left[\frac{\Delta h^o}{h_{fe}} \frac{c_e^2}{(1 + c_e)} \frac{1}{(1 - c_{2e}^2)} \right] \left(\frac{1500}{T_w}\right)^{3.5} \quad (8)$$

It is desired to find \hat{K}_g such that the heat transfer ratio $(q - q_f)/(q_E - q_f)$, obtained by Eq. (7) will match the result given by Goodwin and Chung in terms of Γ_g . It is found that the heat transfer ratios match quite satisfactorily if

$$\hat{K}_g = 21 \Gamma_g \quad (9)$$

Figure 1 shows the comparison between the heat transfer ratio obtained from Ref. 9 and that from Eqs. (7) and (9). It is seen that the present equivalent surface reaction theory represented by Eqs. (1), (7), and (9) predicts the heat transfer ratio satisfactorily for noncatalytic walls.

Let us now consider surfaces of arbitrary catalycity, represented by a specific rate constant K_w , in the presence of nonequilibrium gas phase reaction. The diffusion rate of atoms to the surface must then be equal to the total rate of recombination of atoms by both the gas-phase recombination and the catalytic surface recombination. Equation (1) is generalized for this case as

$$\rho_w D_w \left(\frac{\partial m}{\partial y} \right)_w = K_g \frac{m_w^2}{1 + m_w} + (\rho_w K_w) m_w \quad (10)$$

The solution of Eqs. (2), (10), and (6) for $(q - q_f)/(q_E - q_f)$ with the

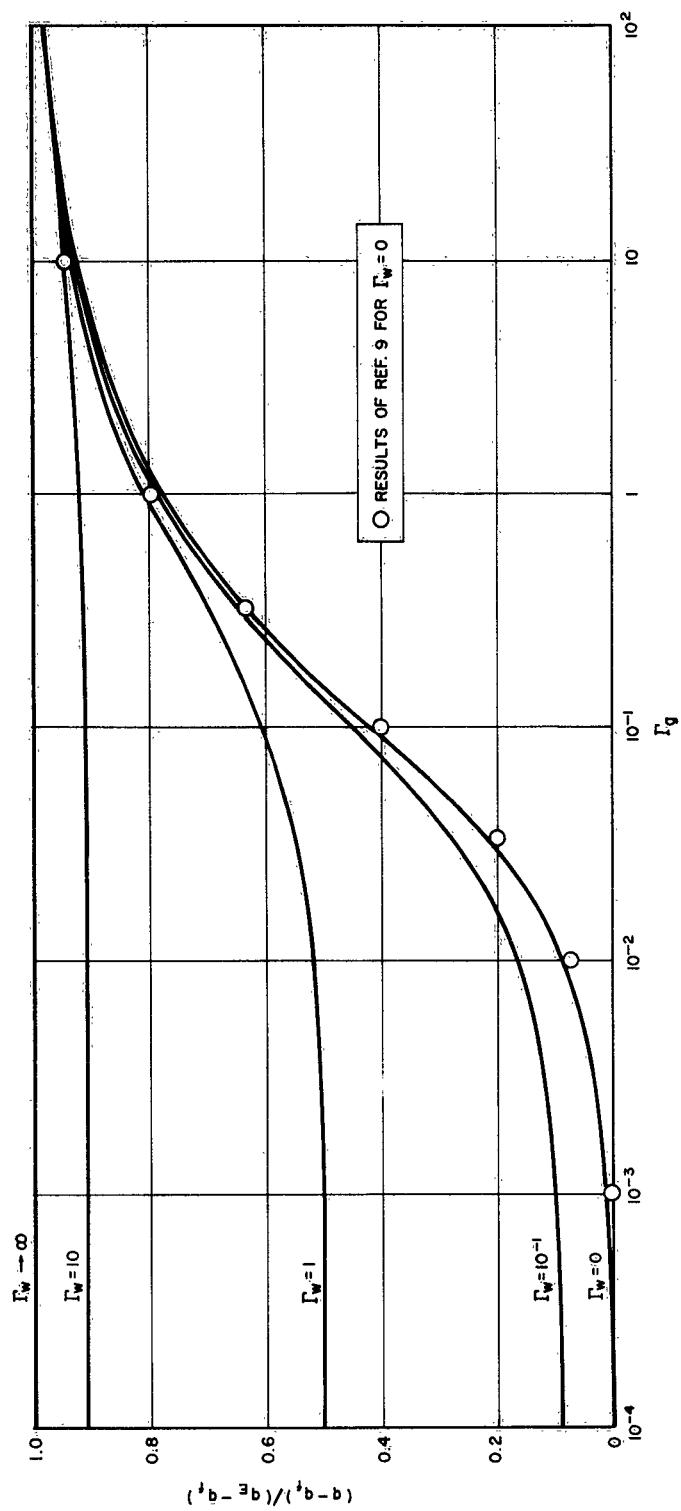


Figure 1. Variation of $(q - q_f)/(q_E - q_f)$ with Respect to Γ_w and Γ_q .

aid of Eqs. (5) and (9) gives

$$\frac{q - q_f}{q_E - q_f} = 1 - \frac{[(\Gamma_w)^2 + 4(1 + \Gamma_w + 21\Gamma_g)]^{1/2} - \Gamma_w}{2(1 + \Gamma_w + 21\Gamma_g)} \quad (11)$$

where for the stagnation region of axisymmetric bodies

$$\Gamma_w = \frac{(\rho_w K_w) Sc^{2/3}}{(0.47)[2(\rho_e \mu_e)_o BC]^{1/2}} \quad (12)$$

Equation (11) is a closed form solution which gives the heat transfer ratio $(q - q_f)/(q_E - q_f)$ for arbitrary-rate simultaneous gas-phase and surface reactions.

The terms Γ_g and Γ_w , defined by Eqs. (8) and (12), are essentially Damkhöler numbers representing the ratio of characteristic diffusion time to characteristic chemical reaction time for the gas-phase and surface reactions, respectively.

DISCUSSION

The accuracy of the solution, Eq. (11), cannot be checked for the arbitrary combinations of Γ_g and Γ_w because the general exact solutions are not available. It can be established that the equation gives correct results at the two limiting cases of either $\Gamma_g = 0$ or $\Gamma_w = 0$. It is sufficiently accurate when $\Gamma_w = 0$ because Γ_g was obtained by matching the results with the solutions of Ref. 9. It is also correct when $\Gamma_g = 0$ because the solution (11) essentially becomes the solution of Ref. 3. Though there is no direct check in the intermediate region, it is felt that the physical reasoning leading to the equivalent surface reaction concept of Eq. (10) is sound. The excellent correlation shown for the gas phase reaction with noncatalytic surface appears to support the accuracy of the results presented.

The variation of $(q - q_f)/(q_E - q_f)$ with respect to Γ_g and Γ_w , as given by Eq. (11) is seen in Fig. 1. The general behavior is similar to that for the Couette flow obtained in Ref. 10.

It is noted here that the same problem considered here is also being studied by Inger* from a different approach. In his analysis the production term, or the source term, in the formal diffusion equation is approximated by a simpler function requiring only a correct matching near the surface. It is therefore based on a concept similar to that used herein in that the chemical state near the surface is assumed to be of controlling influence. It is still, however, an approximate analysis and the accuracies of any of these approximate analyses can be checked only when exact solutions become available.

CONCLUSIONS

The concept of equivalent surface reaction has been developed for gas-phase recombination at the stagnation region of blunt bodies. This concept is based on the fact that the chemical state of a nonequilibrium highly cooled boundary layer is largely determined by the recombination that occurs near the wall. An equation based on this concept was shown to predict the heat transfer to a noncatalytic surface to within a few percent of the more accurate existing results. The equation was generalized to apply to the case in which surface catalytic recombination occurs simultaneously with gas-phase reaction. The present solution, which is in a simple closed form, should be useful in estimating heat transfer although the accuracy of the solution cannot be checked for the general case, due to a lack of exact solutions. The atom concentration profile across the boundary layer can be obtained from the value m_w obtained herein, since in a frozen boundary layer the profile is determined when m_w is known (for instance, see Ref. 3) and the present theory is, in essence, based on the frozen boundary layer theory with modification only in the boundary condition at the surface. The profile thus

*To be published.

obtained should approximate the true profile with the same degree of accuracy as the heat transfer results. This profile, in turn, defines the chemical state across the boundary layer.

The equivalent surface reaction concept will be extended to flow fields beyond the stagnation point of a blunt body.

NOMENCLATURE

- C = $\rho\mu$ ratio defined by Eq. (3)
 c = total atom mass fraction
 c_2 = atom mass fraction of nitrogen atoms
 D = binary diffusion coefficient
 h_f = frozen total enthalpy
 Δh^0 = heat of recombination
 K_g = equivalent surface reaction constant for gas phase reaction
 \hat{K}_g = parameter defined by Eq. (5)
 K_w = specific catalytic surface recombination constant
 k_o = constant portion of recombination coefficient ($= 1.56 \times 10^{20}$)
 $m = c/c_e$
 p = pressure (atmosphere)
 q = heat transfer to surface
 R = universal gas constant ($= 82.06 \text{ cm}^3 \text{ atm/mole } ^\circ\text{K}$)
 r = distance from the axis of symmetry to the surface
 s = function defined by Eq. (3)
 Sc = Schmidt number, $\mu/\rho D$
 T = absolute temperature ($^\circ\text{K}$)
 u = streamwise velocity
 x = streamwise distance
 y = distance normal to surface
 $\beta = (du_e/dx)_o$ (in/sec for Eq. 8)

Γ_g = Damkhöler number for gas-phase recombination

Γ_w = Damkhöler number for surface recombination

$\epsilon = \begin{cases} 0 & \text{for two-dimensional body} \\ 1 & \text{for axisymmetric body} \end{cases}$

η = function defined by Eq. (3)

μ = viscosity

ν = kinematic viscosity, μ/ρ

ρ = density

SUBSCRIPTS

E = equilibrium

e = edge of boundary layer

f = frozen

o = stagnation point

w = wall

∞ = free stream

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